

PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)


(PCT Article 36 and Rule 70)

Applicant's or agent's file reference PC506AG	FOR FURTHER ACTION See Form PCT/IPEA/416	
International application No. PCT/IB2004/002098	International filing date (day/month/year) 24.06.2004	Priority date (day/month/year) 25.06.2003
International Patent Classification (IPC) or national classification and IPC C08F8/00, C08F8/34, C08F8/30, C08F255/02		
Applicant UNIVERSITA' DI PISA et al.		

- This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.
- This REPORT consists of a total of 5 sheets, including this cover sheet.
- This report is also accompanied by ANNEXES, comprising:
 - ☒ sent to the applicant and to the International Bureau a total of 5 sheets, as follows:
 - ☒ sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).
 - ☐ sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.
 - ☐ (sent to the International Bureau only) a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).

4. This report contains indications relating to the following items:

- ☒ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☐ Box No. IV Lack of unity of invention
- ☒ Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☐ Box No. VII Certain defects in the international application
- ☐ Box No. VIII Certain observations on the international application

Date of submission of the demand 25.01.2005	Date of completion of this report 08.07.2005
Name and mailing address of the International preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer Wirth, M Telephone No. +49 89 2399-8595



**INTERNATIONAL PRELIMINARY REPORT
ON PATENTABILITY**

International application No.
PCT/IB2004/002098

Box No. I Basis of the report

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.
- ☐ This report is based on translations from the original language into the following language , which is the language of a translation furnished for the purposes of:
- ☐ international search (under Rules 12.3 and 23.1(b))
 - ☐ publication of the international application (under Rule 12.4)
 - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)
2. With regard to the **elements*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report):*

Description, Pages

1-24 as originally filed

Claims, Numbers

1-24 received on 19.04.2005 with letter of 18.04.2005

- ☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing
3. ☐ The amendments have resulted in the cancellation of:
- ☐ the description, pages
 - ☐ the claims, Nos.
 - ☐ the drawings, sheets/figs
 - ☐ the sequence listing (*specify*):
 - ☐ any table(s) related to sequence listing (*specify*):
4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
- ☐ the description, pages
 - ☐ the claims, Nos.
 - ☐ the drawings, sheets/figs
 - ☐ the sequence listing (*specify*):
 - ☐ any table(s) related to sequence listing (*specify*):

* If item 4 applies, some or all of these sheets may be marked "superseded."

**INTERNATIONAL PRELIMINARY REPORT
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Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	1-24
	No: Claims	
Inventive step (IS)	Yes: Claims	1-24
	No: Claims	
Industrial applicability (IA)	Yes: Claims	1-24
	No: Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

Re Item I

Basis of the report

In claim 16, the trade names Irganox were replaced by the corresponding chemical names. This is considered allowable under Art 34(2)b) PCT.

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. The following document is referred to in this communication:

D1: ROMANI F ET AL: "Monitoring the chemical crosslinking of propylene polymers through rheology" POLYMER, ELSEVIER SCIENCE PUBLISHERS B.V, GB, vol. 43, no. 4, February 2002 (2002-02), pages 1115-1131, XP004312430 ISSN: 0032-3861
D2: EP-A-1 216 999 (BASELL POLIOLEFINE SPA) 26 June 2002 (2002-06-26)
D3: US-A-3 301 837 (GIULIANO BARTORELLI ET AL) 31 January 1967 (1967-01-31)
D4: WONG B ET AL: "Melt rheology of graft modified polypropylene" POLYMER, ELSEVIER SCIENCE PUBLISHERS B.V, GB, vol. 38, no. 11, May 1997 (1997-05), pages 2781-2789, XP004061851 ISSN: 0032-3861

2. D1 discloses a process in which polypropylene is reacted with an initiator and CEFA or BFA which are the preferred "grafting compound" of the present application. D2 and D3 disclose the reaction of polyolefins with unsaturated furanic compounds (claims, examples).

The reaction of an additional unsaturated compound is not disclosed in D1-D3. Present claims 1-24 are therefore novel (Art 33(2) PCT).

The problem to be solved was to avoid the variations in molecular weight of the polymer and to increase the degree of grafting when an unsaturated monomer is

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grafted onto a polyolefin. This problem is solved by the use of the "grafting compound having an electron donator heterocyclic group" (see examples 10-17 of the application).

D1 teaches that in the crosslinking reaction involving radicals, B-cission reactions can be avoided by using appropriate coagents thereby preventing chain degradation. D4 (abstract and second column) points on the fact that the control of B-cission reactions are desirable during the grafting process because they result in a loss of molecular weight. However, neither D1 nor D4 addresses the problem of increase of the degree of grafting. Inventive step is therefore acknowledged (Art 33(3) PCT).

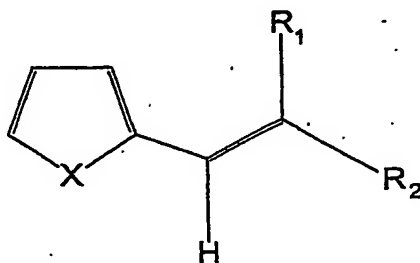
CLAIMS

1. A controlled radical grafting process of a polyolefin, derived from monomeric units comprising α -olefins, comprising the reaction of the polyolefin and at least one radical reaction initiator with a grafting system which comprises at least one grafting compound having an electron donator heterocyclic aromatic ring conjugated to at least one $\text{HC}=\text{CR}_1\text{R}_2$ group in which at least one of R_1 and R_2 is an electron acceptor functional group, wherein $\langle - \rangle$

2. A process according to claim 1, in which R_1 and R_2 are chosen independently of one another from $-\text{H}$, $-\text{COOR}$, $-\text{COOH}$, $-\text{COR}$, $-\text{COH}$, $-\text{CN}$, $-\text{CONH}_2$, $-\text{COO}(\text{CH}_2)_n\text{CF}_3$ and $-\text{COO}(\text{CH}_2)_n\text{CN}$, where R is a linear or branched aliphatic or aromatic linear alkyl group and n is a whole number lying between 1 and 20, with the proviso that R_1 and R_2 are not both $-\text{H}$.

3. A process according to claim 1, in which the said heterocyclic ring is a possibly substituted furanic thiofenic, or pyrrolic ring.

4. A process according to any preceding claim, in which the said grafting system comprises a compound of formula:



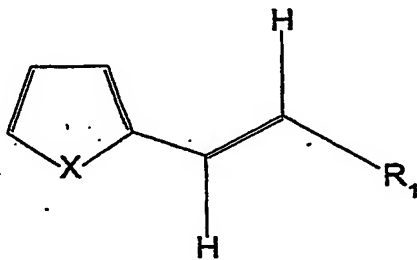
where X is chosen from O , S and N , and R_1 and R_2 are the same or different functional groups chosen from $-\text{COOR}$, $-\text{COOH}$,

-COR, -COH, -CN, -CONH₂, -COO(CH₂)_nCF₃ and -COO(CH₂)_nCN where R is an aliphatic or aromatic linear or branched alkyl group and n is a whole number lying between 1 and 20.

5. A process according to claim 4, in which the said groups R₁ and R₂ are the same of the type -COOR, where R is -CH₂CH₃.

6. A process according to claim 4, in which the said group R₁ is -CN and the group R₂ is -COOR, where R is -CH₂CH₃.

7. A process according to any preceding claim, in which the said grafting system comprises a compound of formula:



where X is chosen from O, S and N, and R₁ is a functional group chosen from -COOR, -COOH, -COR, -COH, -CN, -CONH₂, -COO(CH₂)_nCF₃ and -COO(CH₂)_nCN where R is a linear or branched aliphatic or aromatic linear alkyl group and n is a whole number lying between 1 and 20.

8. A process according to claim 7, in which the said group R₁ is -COOR, where R is -CH₂CH₂CH₂CH₃.

~~9. A process according to any preceding claim, in which the~~
 < said grafting system further includes at least one unsaturated compound which has at least one group which is able to react with an aminic and/or carboxylic and/or hydroxylic functionality and

~~10.~~ A process according to claim ~~9~~, in which the said unsaturated compound is chosen from acrylic and methacrylic compounds, maleic anhydride, derivatives ester of maleic anhydride, and their mixtures.

9 ~~11~~. A process according to any preceding claim, in which the said polyolefin is chosen from the group consisting of homopolymers and copolymers of α -olefins and their mixtures.

10 ~~12~~. A process according to any preceding claim, in which the said radical initiator has a half life lying between 10 and 200 seconds in the temperature range lying between 120 and 240°C.

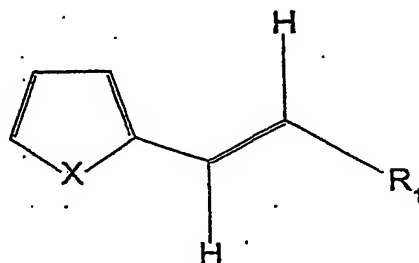
11 ~~13~~. A process according to any preceding claim, in which the said radical initiator is an organic peroxide such as a dialkyl peroxide, a diacyl peroxide, a peroxy ester or a peroxychetal.

12 ~~14~~. A process according to any preceding claim in which the said radical initiator is chosen from the group consisting of dicumil peroxide, ditertbutyl peroxypropylbenzene, 2,5 dimethyl 2,5 ditertbutyl peroxy-hexane, 3,6,9-triethyl-3,6,9 trimethyl-1,4,7 - triperoxynonan and their mixtures.

13 ~~15~~. A process according to any preceding claim, in which 0.5 to 30% by weight of the said grafting system and from 0.05 to 5 parts by weight of the said radical initiator are mixed with 100 parts by weight of the said polyolefin.

14 ~~16~~. A process according to claim 1, in which 100 parts by weight of the said polyolefin are mixed with 1 - 25 parts by weight of an unsaturated compound chosen from acrylic and

methacrylic compounds, maleic anhydride, ester derivatives of maleic anhydride and their mixtures, 0.05 - 5 parts by weight of a radical initiator of organic peroxide type and 0.1 - 5 parts by weight of a compound of formula



where X can be chosen from O, S and N, and R₁ is a functional group chosen from COOR, -COOH, -COR, -COH, -CN, -CONH₂, -COO (CH₂)_nCF₃ and -COO(CH₂)_nCN, where R is a linear or branched aliphatic or aromatic alkyl group and n is a whole number lying between 1 and 20.

15 ¹³ 11. A process according to claim ¹⁴ 13 or claim ¹⁴ 14, in which 100 parts by weight of the said polyolefin are further mixed with 0.01-1 parts by weight of a radical reaction inhibitor.

16 ¹⁵ 18. A process according to claim ¹⁵ 17, in which the said radical reaction inhibitor is chosen from the group consisting of 3,5-di-tert-butyl-4 hydroxytoluene, Irganox 1010 and Irganox 1076, pentaerythrityl-tetraakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate] and octadecyl 3,5-di-(tert)-butyl-4-hydroxy

17 ¹⁶ 19. A process according to any preceding claim, performed in ¹⁷ hydro cinnamate a mixer provided with a rotor.

18 ¹⁷ 20. A process according to claim ¹⁷ 19, in which the said grafting system is introduced into the mixer after the polyolefin.

¹⁸

~~19~~²¹. A process according to claim ~~20~~¹⁸, in which the said grafting system is introduced into the mixer once the torque transmitted by the rotor member is stabilised.

¹⁷¹⁹

~~20~~²². A process according to claims from ~~18~~¹⁷ to ~~21~~¹⁹, in which the said radical initiator is introduced subsequently to the grafting system.

¹⁷²⁰

~~21~~²³. A process according to any of claims from ~~18~~¹⁷ to ~~22~~²⁰, in which the rotor member turns with an angular velocity of 20 - 70 rpm.

¹⁷²¹

~~22~~²⁴. A process according to any of claims from ~~18~~¹⁷ to ~~23~~²¹, in which the residence time of the reagents in the mixer lies between 5 and 30 minutes.

¹⁷²²

~~23~~²⁵. A process according to any of claims from ~~18~~¹⁷ to ~~24~~²², in which the temperature of the reagents lies between 120 and 230°C.

¹⁷²³

~~24~~²⁶. A process according to any of claims from ~~18~~¹⁷ to ~~25~~²³, performed continuously by means of a twin screw extruder.